

Synthesis of a novel magnetic photocatalyst by direct deposition of nanosized TiO_2 crystals onto a magnetic core

S. Watson, D. Beydoun, R. Amal*

Centre for Particle and Catalyst Technologies, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales (UNSW), Sydney, NSW 2052, Australia

Received 24 July 2001; received in revised form 9 January 2002; accepted 9 January 2002

Abstract

This paper presents the preliminary results of a study in which nanocrystalline titanium dioxide particles were directly coated onto a magnetic core. A modified hydrolysed alkoxide process, in which the hydrolysis and condensation of a titanium alkoxide (titanium isopropoxide) was carried out under acidic conditions, using a large water:alkoxide ratio, allowed for the synthesis of crystalline titanium dioxide at relatively low temperatures (90°C). This method is attractive since it eliminated a high-temperature heat treatment step required in a typical sol–gel method, which is needed to transform the amorphous titanium dioxide formed into a photoactive crystalline phase. The prepared particles were photoactive as well as being easy to separate from a slurry-type photoreactor under the application of an external magnetic field. The application of the sol–gel process for the deposition of a crystalline coating of titanium dioxide onto fine particles has never been attempted before. Thus while this approach is envisaged to be quite challenging, its success will provide new fundamental knowledge and tremendous opportunities for the synthesis of tailored particles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nanocrystalline; Titanium dioxide; Magnetic photocatalyst; Sol–gel processing

1. Introduction and background

Modifying the properties of one material by coating it with another type of material has been a popular approach widely documented in the literature [1–8]. In this work, the concept of coating one material with another is used to develop a novel magnetic photocatalyst. The photocatalyst is produced by coating a layer of the photoactive material titanium dioxide onto the surface of a magnetic core. In this case, both the core and the shell are of interest. The magnetic core is useful for enhancing the separation properties of suspended particles from solution, whereas the photocatalytic properties of the outer titanium dioxide are used to destroy organic contaminants in wastewaters.

Titanium dioxide-mediated photocatalytic detoxification of wastewater is a process which combines heterogeneous catalysis with solar technologies. It is a promising technology through which a wide spectrum of organic contaminants may be degraded or completely mineralised. Photocatalysts used in UV or near-UV light-activated processes are typically semiconductor materials such as TiO_2 , ZnO or CdS .

Titanium dioxide is the semiconductor which provides the best compromise between catalytic performance and stability in aqueous media and is by far the material most commonly used as a photocatalyst.

There are a number of methods available for preparing titanium dioxide photocatalysts. These preparation methods can be classified into two categories: the wet chemistry methods, such as the sol–gel technique, and the dry methods, such as the aerosol technique. On a commercial scale, titanium dioxide powder is manufactured primarily by a flame aerosol process [9]. The various synthesis routes to produce titania powders, include the sulphate process, the chloride route, the sol–gel method which involves the hydrolysis of titanium organic compounds, vapour-phase pyrolysis, and inert gas condensation [10].

The wet methods (conventional sol–gel process) are the most common of the techniques for particle coating. These are based on the precipitation of the coating material onto colloids suspended in solutions of the corresponding chemicals [7]. The preparation of coated particles using the hydrolysed alkoxide process has been thoroughly investigated. Emphasis has been placed on producing systems in which a layer of a uniform, controllable thickness can be deposited [3], with an ultimate aim to tailor desired characteristics into the final coated particles.

* Corresponding author. Tel.: +61-29385-4361; fax: +61-29385-5596.
E-mail address: r.amal@unsw.edu.au (R. Amal).

Sol–gel processing generates inorganic oxides via gelation, precipitation or hydrothermal treatment [11]. It involves the use of molecular precursors, either an inorganic salt or a metal alkoxide, as starting materials [12]. The reaction between the precursor material and water is a two-step process and involves a hydrolysis reaction and a condensation (or polymerisation) reaction. The hydrolysis results in the formation of a M–OH bond while the condensation reaction occurs once the OH groups are created [13]. Typically, the titanium dioxide deposited using the sol–gel process is amorphous in nature. This amorphous form is not photoactive [14,15]. Therefore heat treatment, which leads to the crystallisation of the hydrous titanium dioxide, is an essential step in the preparation of the photocatalyst samples.

For the past few years, we have been working on the synthesis of stable magnetic titanium dioxide photocatalyst [16–20]. The original synthesis method adopted up to this stage involved the deposition of the titanium dioxide coating using the conventional sol–gel method which resulted in a coating which was amorphous in nature. Therefore heat treatment, which leads to the crystallisation of the hydrous titanium dioxide into a photoactive semiconductor state, was an essential step in the preparation of the photocatalyst samples. From our studies thus far the heat treatment step was identified as a key step in determining the final properties of the prepared samples as it was shown to be detrimental to both photoactivity and magnetic properties [17,21].

A number of processes occur during the heat treatment of the coated samples which have important implications with regard to the photoactivity and the magnetic properties of the prepared catalyst particles [17,21]. The heat treatment step was found to lead to a decline in surface area (due to sintering and crystal growth) and a loss in surface hydroxyl groups. Excessive heat treatment of iron oxide/titania systems (without the insulative silica layer) also led to interactions between the magnetic core and the titania coating. At the same time, due to the porosity of the coating, the heat treatment also resulted in partial oxidation of the magnetic iron oxide core, and hence a decrease in the magnetic properties of the prepared photocatalysts. Waite [22] suggested that the occurrence of faults and dislocations during the heat treatment step were also likely to lead to a decrease in photoactivity.

Thus an alternative particle preparation method was sought in which the heat treatment step was not required. In the literature, the formation of crystalline TiO₂ particles following the sol–gel route under acidic conditions had been reported [13,23–25]. This modified sol–gel method, as outlined by Gopal et al. [13], involved the hydrolysis and condensation of a titanium alkoxide in an acidic medium while using a very high water:alkoxide ratio in a system. Thus in this study, a preliminary investigation into the coating of nanosized crystalline TiO₂ directly onto a magnetic core is presented. To the best of our knowledge, this is the first study to present the coating of crystalline material directly onto magnetic core particles. It is also the

first study to present the use of directly deposited crystalline TiO₂ (calcination) as photocatalysts.

2. Experimental

All chemicals used were reagent grade and prepared in deionised, distilled water.

2.1. Particle preparation

Colloidal, hexagonal platelet magnetite particles 40–70 nm in size were prepared by a procedure presented by Sugimoto and Matijevic [26]. This involved the ageing of Fe(OH)₂ gels at 90 °C in the presence of KNO₃ [27]. The preparation of the magnetic photocatalyst particles involves two coating steps. The first step was to encapsulate the magnetite particles within a silica shell to produce Fe₃O₄/SiO₂ particles. This is necessary to ensure the stability of the particles against dissolution under irradiation [17,18]. The second step in preparing the photocatalyst particles was to coat the Fe₃O₄/SiO₂ particles with a photoactive titanium dioxide layer.

2.1.1. Preparation of silica dioxide-coated magnetite particles

The Fe₃O₄/SiO₂ particles were obtained using the conventional sol–gel process as described by the following procedure (a summary of the concentrations used is given in Table 1). Ethanol, ammonia and magnetite sols were mixed. 0.16 g of magnetite was dispersed in 11.4 ml of milli-Q water. A required volume of tetraethyl-orthosilicate (TEOS) was added to the mixture dropwise while it was being stirred by an overhead stirrer in a constant temperature 20 °C water bath. The reaction mixture was aged for 5 h and the silica-coated magnetite particles were recovered and washed by centrifugation and redispersion three times with ethanol. These particles were then allowed to dry in the oven at 60 °C overnight before being coated with titanium dioxide.

2.1.2. Preparation of titanium dioxide-coated Fe₃O₄/SiO₂ particles

The next step of preparing the magnetic photocatalyst involved coating the insulated Fe₃O₄/SiO₂ particles with a titanium dioxide layer to produce Fe₃O₄/SiO₂/TiO₂ particles. Two different procedures were used. The first procedure involved the deposition of an amorphous TiO₂ coat-

Table 1
Concentrations used to prepare the Fe₃O₄/SiO₂ particles

Component	Concentration
Fe ₃ O ₄ (g/l)	0.2
H ₂ O (M)	0.51
NH ₄ OH (M)	0.79
TEOS (M)	0.0037
Ethanol (M)	15

Table 2

Concentrations used to prepare the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ (amorphous) particles (sample FSTH)

Component	Concentration
$\text{Fe}_3\text{O}_4/\text{SiO}_2$ (g/l)	0.25
H_2O (M)	0.40
TBOT (M)	0.005

ing, followed by calcination (high-temperature heat treatment). The second procedure involved the direct deposition of crystalline titanium dioxide onto the magnetic core. Each of these procedures is described below.

2.1.2.1. Deposition of an amorphous TiO_2 onto $\text{Fe}_3\text{O}_4/\text{SiO}_2$ followed by calcination. Titanium dioxide was deposited onto the silica-coated magnetite particles ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) through the hydrolysis and condensation of titanium butoxide (TBOT). A summary of the concentrations used is given in Table 2. A measured amount (0.1 g) of silica-coated magnetite particles was dispersed in 25 ml of ethanol in an ultrasonic bath for 30 min. This suspension was then transferred into a reaction vessel containing the required amount of water which had been separately mixed in ethanol. The resulting mixture was kept at 8 °C. A predetermined amount of TBOT, giving a final concentration of 0.005 M, was dissolved in 40 ml ethanol and then added to the magnetite/water/ethanol mixture. This reaction mixture was immediately placed in a 20 °C water bath with continuous stirring using an overhead stirrer. The mixture was aged for 3 h and the titania-coated particles were recovered and washed by centrifugation and redispersion three times with ethanol, followed by two times with water. These particles were then allowed to dry in the oven at 60 °C for 2 days, and stored ready to be heat treated.

The amorphous coating of titanium dioxide formed was transformed to a crystalline phase by calcining the particles in a tubular furnace in the presence of air. The sample was placed in an electric tubular furnace at ambient temperature. The furnace was then switched on and set to the desired temperature. The temperature increased at a rate of approximately 8 °C/min. Upon reaching 450 °C temperature, the particles were left in the furnace for 3 h. Air was slowly circulated through the furnace through a small vent hole. The sample was referred to as FSTH.

2.1.2.2. Direct deposition of a nanocrystalline TiO_2 coating onto $\text{Fe}_3\text{O}_4/\text{SiO}_2$. Crystalline titanium dioxide was deposited onto silica-coated magnetite particles ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) through the hydrolysis and condensation of titanium isopropoxide. A summary of the concentrations used is given in Table 3. A measured amount of silica-coated magnetite particles was dispersed in 50 ml of water in ultrasonic bath for 30 min. This suspension was then transferred into a reaction vessel. Predetermined amounts of water/propanol/ HNO_3 were introduced into the vessel. After the resulting mixture

Table 3

Concentrations used to prepare the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ (crystalline) particles (sample FSTCu)

Component	Concentration
$\text{Fe}_3\text{O}_4/\text{SiO}_2$ (g/l)	0.25
H_2O (M)	45.2
HNO_3 (M)	0.56
2-Propanol (M)	0.73
Titanium isopropoxide (M)	0.06

was dispersed, it was placed in a 90 °C ultrasonic bath. A predetermined amount of titanium isopropoxide was added dropwise to the insulated magnetite/water/propanol/ HNO_3 mixture (kept at 90 °C). The reaction mixture was aged for 30 min after which it was quenched with an equal volume of ethanol (to stop the reaction). The particles were recovered and washed by centrifugation and redispersion three times with ethanol, followed by two times with water. These particles were then allowed to dry in the oven at 60 °C for 2 days. The sample prepared following the procedure described above, these are referred to as FSTCu. In order to study the effect further heating this sample, aliquots were taken and additionally dried at 60, 100 or 150 °C for 5 h. These samples were referred to as FSTCu(60), FSTCu(100) and FSTCu(150), respectively.

2.1.3. Characterisation and photoactivity testing of the prepared particles

The samples were characterised using transmission electron microscopy and scanning transmission electron microscopy (STEM). The instrument used was a Phillips CM200 electron microscope at 200 kV. Transmission electron microscopy was used to obtain information regarding the size and shape of the core and coated particles as well as thickness of the deposited titanium dioxide layer. The STEM was supported by elemental X-ray mapping images taken using an EDX (energy-dispersive X-ray) spectrometer. XRD analysis was used to identify the phases present in the catalyst using $\text{Cu K}\alpha$ radiation in a Siemens D5000 diffractometer. XRF analysis was used to determine the composition of the samples. The size distribution of the particles were obtained from photon correlation spectroscopy (PCS) using the dynamic light scattering technique (Brookhaven system). The particle concentration was 0.02 g/l. The ionic strength of the suspension was controlled at 1 mM using KCl.

A series of photoactivity tests were conducted to compare the performance of the different samples prepared. The photocatalytic activity of the prepared particles was assessed using a small batch photocatalytic reaction system which consisted of a photoreactor with a near-UV illumination source (peak wavelength at 380 nm) and a conductivity monitor for measuring carbon dioxide. The catalyst loading was 0.02 wt.% and the system was equilibrated with ambient atmosphere. The photo-oxidation of either 0.25 or 1 μg of

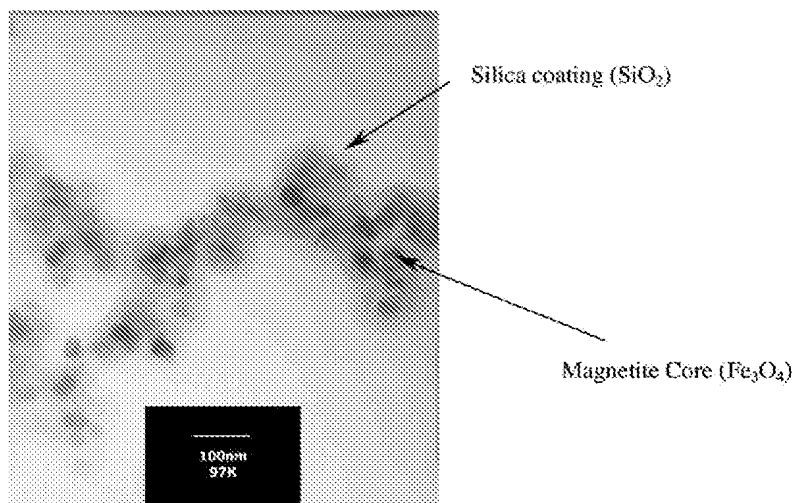


Fig. 1. TEM micrograph of Fe₃O₄/SiO₂ samples prepared using the conventional sol–gel process.

carbon, added as sucrose to a 30 ml suspension of the photocatalyst was used as the test reaction. By monitoring the rate of formation of carbon dioxide, the rate of mineralisation of the sucrose was determined. The initial temperature of suspension was room temperature. The temperature was not monitored during the reaction.

3. Results

3.1. Particle preparation

The coating of the colloidal magnetite with a silica layer involved the coating of a magnetite aggregate due to mag-

netic attraction between the particles. A TEM micrograph of the obtained Fe₃O₄/SiO₂ systems clearly shows the magnetite particles encapsulated in a uniform silica coating (refer to Fig. 1).

3.1.1. Formation of the amorphous titanium dioxide coating

The conventional sol–gel process, which involved ageing ethanolic solutions of TBOT and water in the presence of Fe₃O₄/SiO₂ particles, resulted in the formation of Fe₃O₄/SiO₂/TiO₂ particles, with a thick layer of titania coating being observed. These particles are shown in Fig. 2. The amorphous nature of the titania nature formed using this method was confirmed by the characterless XRD spectra exhibited by these particles.

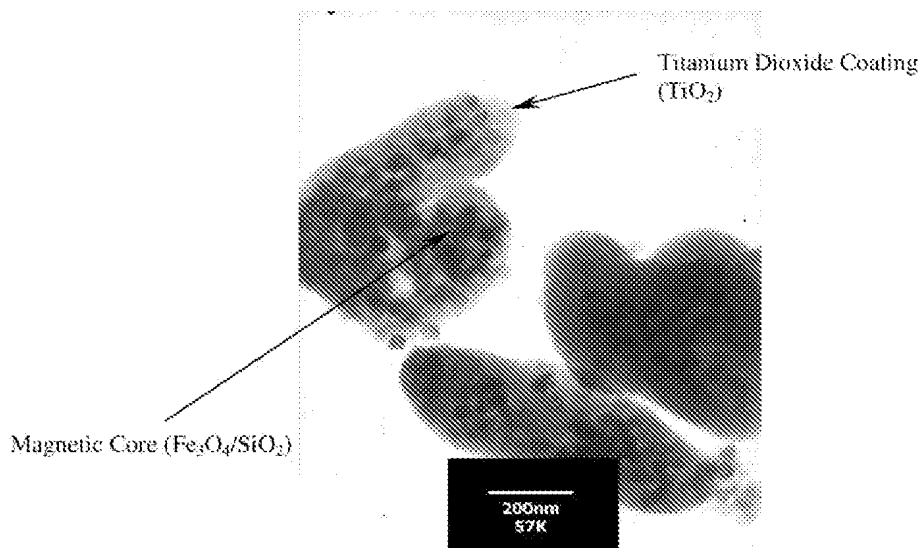


Fig. 2. TEM micrograph of Fe₃O₄/SiO₂/TiO₂ (amorphous) particles (sample FSTH) prepared using the conventional sol–gel process.

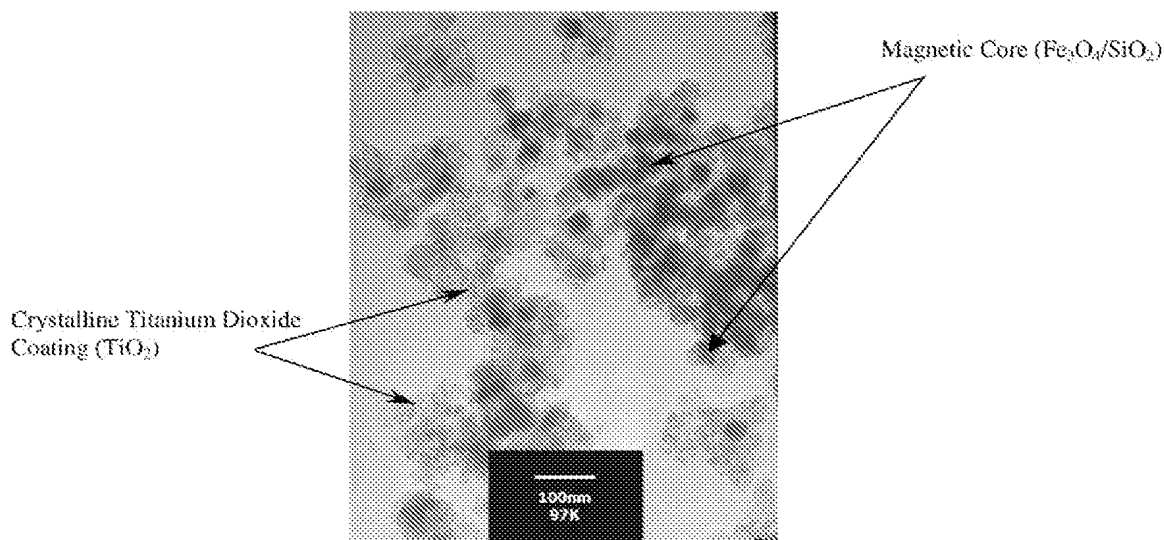


Fig. 3. TEM micrograph of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ (crystalline) particles (sample FSTCu) prepared using the conventional sol-gel process.

3.1.2. Formation of the crystalline TiO_2 coating

Upon the addition of titanium isopropoxide, the reaction mixture became cloudy, but within 4 min it became clear again. As the reaction mixture was aged, the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles suspended became grey in colour. TEM analysis of the particles (Fig. 3) showed clusters of TiO_2 crystals

partially covering the surface of the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ particles as patches. Elemental X-ray mapping of the particles also confirms these results (refer to Fig. 4).

The XRD results are given in Fig. 5. For the coated sample heat treated at 450°C (FSTH), the XRD spectra confirmed the crystalline nature of the titanium dioxide present

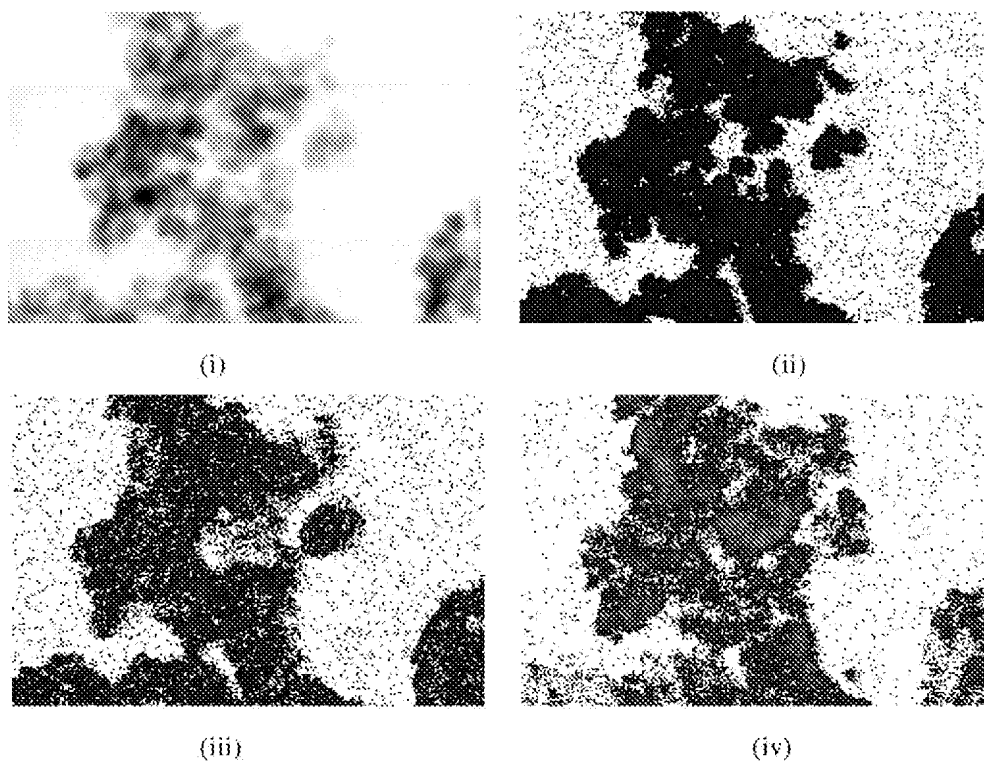


Fig. 4. $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ (crystalline) system: (i) STEM image of particles; (ii) corresponding Fe X-ray map; (iii) corresponding Si X-ray map; (iv) corresponding Ti map.

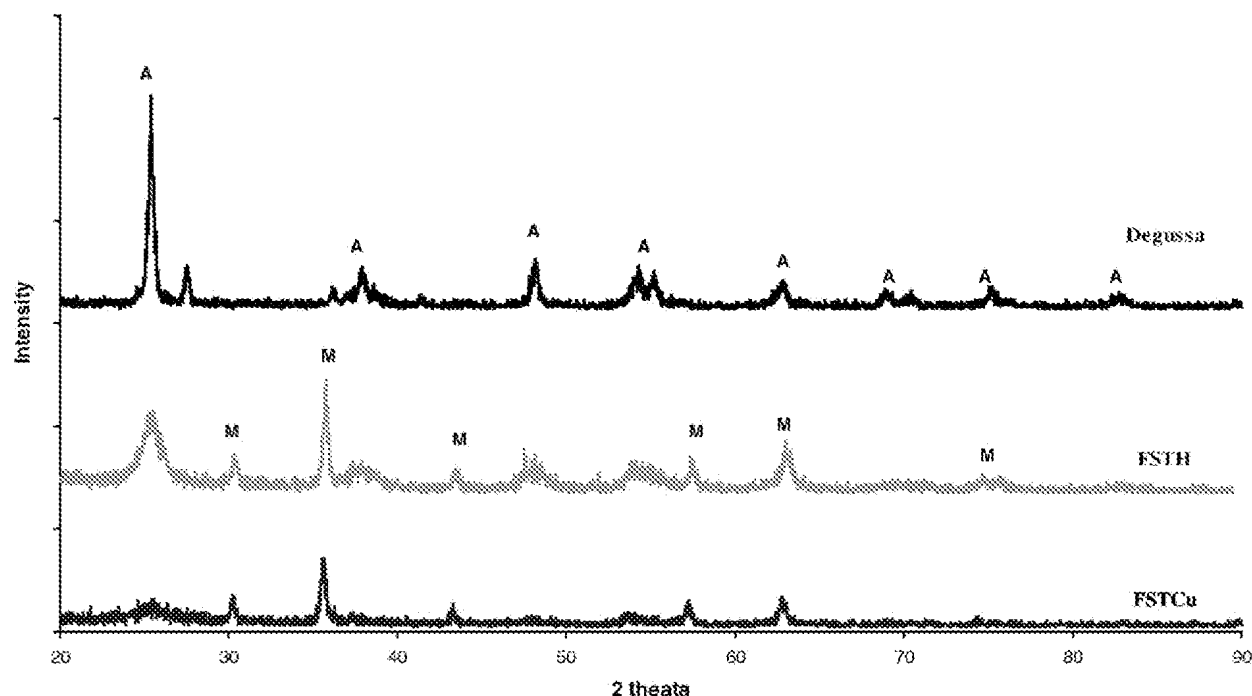


Fig. 5. XRD patterns of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ (crystalline) system prepared the modified sol–gel process (FSTCu), $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ heat treated at 450°C for 3 h (FSTH), and Degussa P25. A: anatase (25.25° , 37.76° , 48.2°); M: magnetite (35.46° , 62.32° , 30.08°).

with anatase being the main crystalline phase present. For the coated sample prepared using the modified sol–gel procedure (FSTCu), the anatase structure was also evident, although the intensity of the peak was very weak. The broader and less intense peaks of this sample when compared with the sample heat treated at 450°C for 3 h (FSTH) may be indicative of smaller crystal size and poorer crystal structure [23]. For both the coated samples (FSTCu and FSTH), peaks can also be seen for the magnetite core, even though the magnetite core had been completely encapsulated within a SiO_2 shell before the deposition of the TiO_2 coating.

3.2. Photoactivity test results

The results of the first set photoactivity tests are given in Fig. 6. A description of the samples tested is given in Table 4. The photocatalytic performance of the particles was compared on the basis of the rate of carbon dioxide generated as the organic substrate (equivalent to $25\ \mu\text{g}$ of carbon added as sucrose) was oxidised. As can be seen from Fig. 6, all the samples tested were photoactive, with the coated sam-

ples prepared using the modified sol–gel process (FSTCu) exhibiting comparable photoactivity to the sample which had undergone heat treatment (FSTH). Both the coated samples had slightly lower photoactivity than the commercially available photocatalyst Degussa P25.

Fig. 7 gives the results of photoactivity testing experiments in which the organic substrate concentration was increased to $100\ \mu\text{g}$ of carbon. Under these conditions, sample FSTCu was found to have lower photoactivity than the heat-treated sample (FSTH), and both these samples again had lower photoactivities than Degussa P25.

In order to study the effect further heating on the photocatalytic performance of sample FSTCu, aliquots were taken and additionally dried at 60 , 100 or 150°C for 5 h. These samples were referred to as FSTCu(60), FSTCu(100) and FSTCu(150), respectively. The results of the photoactivity testing carried out on these samples are given in Fig. 8. A description of the samples tested is given in Table 5. When comparing the photoactivity of FSTCu and FSTCu(60) and FSTCu(100), it can be clearly seen that the photoactivity increased as further heat treatment (even under mild

Table 4
Details of the samples used in the photoactivity tests

Sample code	Sample description	Composition (mass%)	Diameter (nm)	Specific surface area (m^2/g)
Degussa	Commercial TiO_2 photocatalyst	TiO_2 : 100	249	55
FSTCu	$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$, crystalline, prepared using the modified-sol–gel process	Fe_3O_4 : 27; SiO_2 : 20; TiO_2 : 53	1089	300
FSTH	$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{TiO}_2$ calcined at 450°C for 3 h	Fe_3O_4 : 29; SiO_2 : 28; TiO_2 : 43	745	46

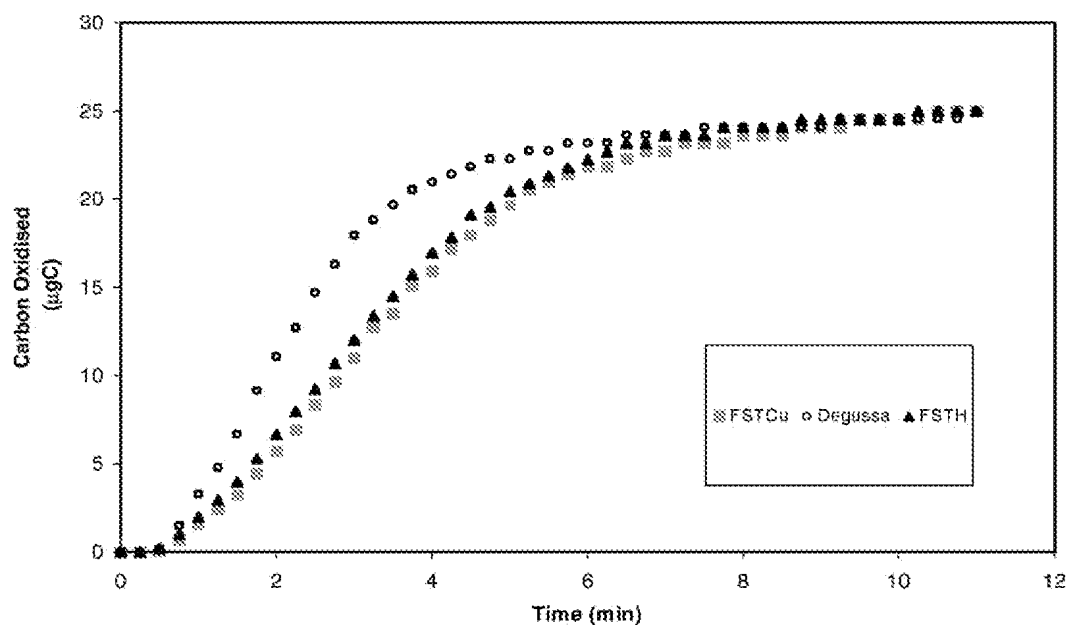


Fig. 6. Results of photoactivity testing comparing the activities of different samples for the degradation 25 µg of carbon. A description of the samples tested is given in Table 4.

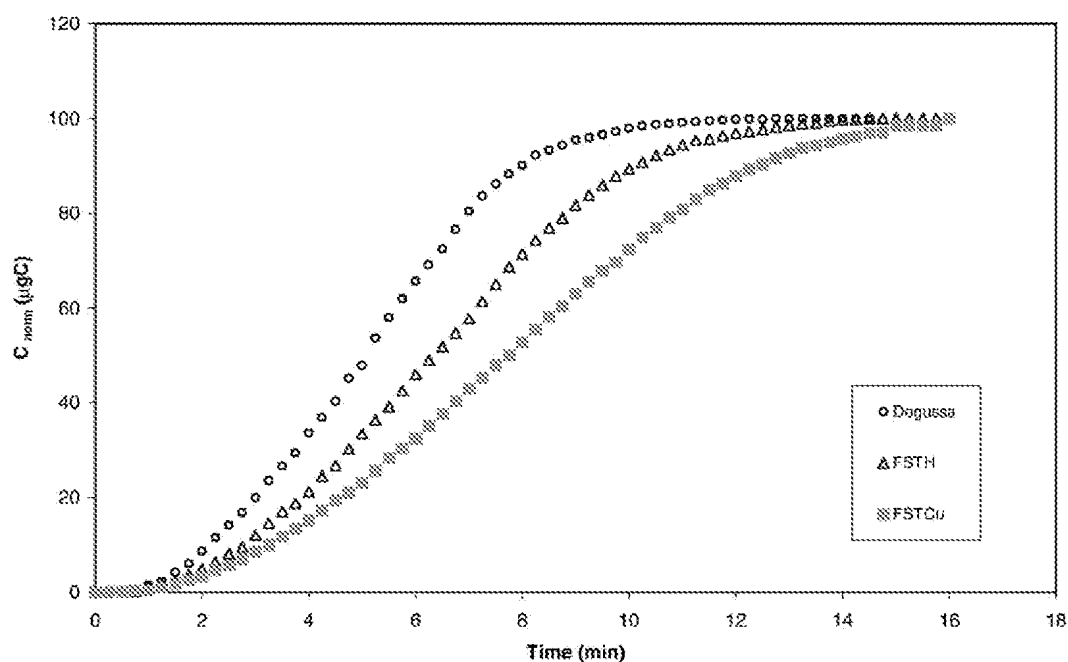


Fig. 7. Results of photoactivity testing comparing the activities of different samples for the degradation 100 µg of carbon. A description of the samples tested is given in Table 4.

Table 5

Details of the samples used in the photoactivity tests to study the effect of further heat treatment

Sample code	Sample description
FSTCu	Fe ₃ O ₄ /SiO ₂ /TiO ₂ , crystalline, prepared using the modified-sol-gel process, recovered using centrifuge, dried in oven at 60 °C overnight
FSTCu(60)	Fe ₃ O ₄ /SiO ₂ /TiO ₂ , crystalline, prepared using the modified-sol-gel process; additional drying for 5 h at 60 °C
FSTCu(100)	Fe ₃ O ₄ /SiO ₂ /TiO ₂ , crystalline, prepared using the modified sol-gel process; additional drying for 5 h at 100 °C
FSTCu(150)	Fe ₃ O ₄ /SiO ₂ /TiO ₂ , crystalline, prepared using the modified sol-gel process; additional drying for 5 h at 150 °C
FSTH	Fe ₃ O ₄ /SiO ₂ /TiO ₂ calcined at 450 °C for 3 h
Degussa	Commercial TiO ₂ sample

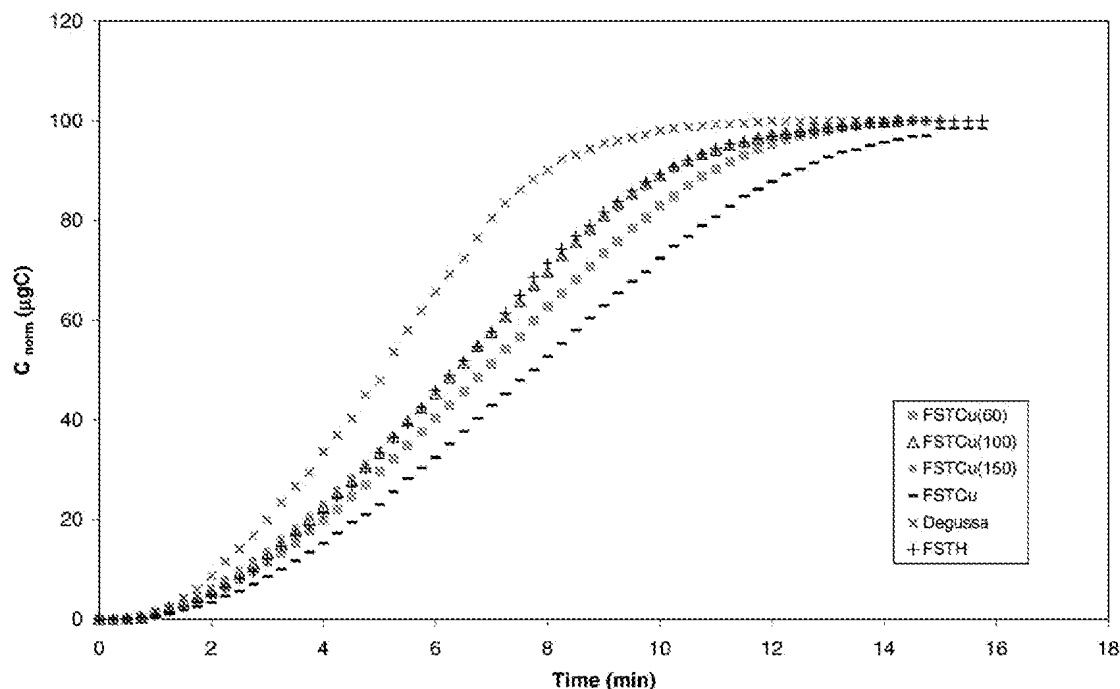


Fig. 8. Results of photoactivity testing comparing the activities of different FSTCu samples undergoing further heat treatment. The tests carried out involved the degradation 100 µg of carbon. A description of the samples tested is given in Table 5.

conditions) was applied. While the sample heat treated further at 150 °C (sample FSTCu(150)) also displayed an improvement in photoactivity compared to sample FSTCu, this improvement was comparable to that achieved when further heat treating at 100 °C (sample FSTCu(100)).

4. Discussion

Anatase titanium dioxide has been found to be the most active crystalline phase of titanium dioxide. Hence the preliminary investigations conducted into the direct coating of insulated magnetite particles with a crystalline titanium dioxide phase aimed at producing nanocrystalline anatase TiO₂. According to Gopal et al. [13], in order to obtain titanium dioxide particles having an anatase structure, the acid catalysed system of titanium isopropoxide and water needed to be heated to 90 °C rapidly. Hence the coating procedure used the same reactant concentrations and rapid heating to 90 °C, in the presence of Fe₃O₄/SiO₂ seed particles.

When seed particles exist in solution while other particles are being deposited, the existence of the seed particles creates a new scenario for the precipitation and formation of the new phase. As the new phase precipitates, three processes can occur. First, the reactants can adsorb on the surface of the seed particles, and the new phase can directly precipitate on the seed particles. Secondly, the new precipitated phase can originate as nanosized particles, precipitated separately in solutions (homogeneous precipitation), which then interact with and adhere to the surface of the seed particles [7,28].

Finally, the new phase may form with minimal interaction with the seed particles. When this occurs, the end result is a mixed system in which the seed particles and the newly precipitated phase coexist as separate phases [1,7,29,30].

As can be seen from Figs. 3 and 4, the presence of the Fe₃O₄/SiO₂ resulted in titania-coated cores (Fe₃O₄/SiO₂/TiO₂ particles). From examining the TEM micrographs, it is postulated that the coating process predominately occurred through a uniform heterocoagulation of precipitated TiO₂ particles with the seed particles due to a difference in the magnitude of their surface charges. The appearance of the coating is consistent with this postulation. An inspection of the coated particles under the electron microscope (Fig. 4), particularly near the edges of the particles showed that the surface of the coated particles is quite rough, and that the particles are composed of smaller subunits. Knowing that a smooth surface indicates a dominance of surface nucleation and growth process [8] this provided strong evidence to suggest that a heterocoagulation mechanism prevailed in the present system, whereby nanosized TiO₂ subunits had adhered to the surface of the magnetic core. The homogeneous precipitation of titanium dioxide using the same reactant concentrations and under the same experimental conditions, in the absence of seed particles, provided further support to the above postulation.

The titanium dioxide did not, however, form a complete coverage of the cores, but occurred in patches on the surface. XRD results shown in Fig. 5 confirmed that the conditions chosen for the preparation of these particles (FSTCu) did result in the deposition of anatase TiO₂ nanocrystals,

although their degree of crystallinity was weak, as can be seen from the low intensity of the anatase peak. The low signal registered could also be contributed by the low amount of anatase.

The formation of the anatase phase of titanium dioxide under acidic conditions and a high water to alkoxide ratio can be explained as follow. The reaction between the alkoxide and water can be considered as a two-step process, a hydrolysis reaction and a condensation reaction. During the conventional sol–gel process, the metal alkoxide reacts with the water, leading to the formation of amorphous hydroxides and hydrous oxides. This in turn can be converted to crystalline oxide by heating. The direct synthesis of crystalline titanium dioxide using the sol–gel process is based on the assumption that complete hydrolysis needs to occur before the condensation reaction begins, and the condensation reaction needs to proceed slowly for the molecules to crystallise into an equilibrium state [13]. Gopal et al. [13] give a thorough discussion of the mechanisms involved. They concluded that complete hydrolysis followed by slow condensation can be effected by processing at a low pH with the crystal structure and shape of the precipitate being dependent on the reaction kinetics. From the results we have presented, we showed that by introducing seed particles into the system, the experimental conditions described above can be extended to produce coated particles in which weakly crystalline titanium dioxide can be directly deposited onto the surface of the cores.

While the titanium dioxide did not form a uniform coating on the surface of the magnetic cores, the presence of TiO_2 in these particles was sufficient to allow for their use as photocatalysts. Experiments were therefore carried out to confirm their photoactivity as well as make a comparison to those which had undergone heat treatment (FSTH). This was needed to verify whether this new preparation method could be adopted to produce photoactive magnetic catalyst particles.

The first set of photocatalytic activity testing experiments involved testing the photoactivity of these particles for the mineralisation of 25 μg of carbon added as sucrose. These results (shown in Fig. 6) demonstrated the photoactivity of sample prepared using the modified sol–gel process (sample FSTCu), with the sucrose present in the system being completely oxidised within 14 min of reaction time. This sample also exhibited comparable photoactivity to the sample which had undergone heat treatment (FSTH).

This was an interesting finding since these two samples did in fact have different properties, in terms of the degree of crystallinity (as found from the XRD results, given in Fig. 5) as well as particle size and composition (refer to Table 4). It was postulated that the concentration of the substrate (sucrose) being used was too low to be able to differentiate between the performance of the coated samples FSTCu and FSTH. It is envisaged that both FSTCu and FSTH had sufficient active sites to degrade the 25 μg of carbon added to the system. While the number of active sites may have dif-

fered, this was not detectable and was not reflected in the photoactivity results. At this low solute concentration, the maximum capacity of the catalyst is yet to be reached. However, Degussa P25 performs better due to its smaller particle size (refer to Fig. 6 and Table 4).

In order to differentiate between the activities of FSTCu and FSTH, the photocatalytic reactions were repeated under conditions in which the surface saturation point by the organic was reached. Under these conditions, the performance of the photocatalyst is influenced by the chemical and surface properties of the photocatalyst itself (i.e. the degradation process becomes chemical reaction controlled). Hence, another set of photoactivity testing experiments was carried out in which the concentration of the substrate (sucrose) was increased to 100 μg of carbon. The results of these experiments are given in Fig. 7.

As can be seen from these results, by increasing the concentration of the organic in the system, a difference was in fact detected between the samples prepared using the modified hydrolysed alkoxide procedure (FSTCu) and the samples in which a heat treatment step was required (FSTH), with sample FSTCu having a lower photoactivity. In systems containing higher substrate concentrations, the catalyst properties begin to play a more significant role in the reaction kinetics. Hence from these conditions, it can be concluded that the sample heat treated at 450 °C for 3 h possessed more favourable photocatalytic characteristics than the sample prepared using the modified hydrolysed alkoxide procedure.

It is interesting to note that the particle size did not reflect the specific surface area (Table 4). The specific surface area measurements can be explained as follows. The higher than expected surface area (given the larger particle size) for sample FSTH is due to the roughness of the surface while the large surface area of sample FSTCu is due to the porosity of the particles. The poor performance of FSTCu particles cannot be explained by specific surface area.

Two postulations are put forward regarding the poor performance FSTCu. Firstly, from the transmission electron microscope analysis it was clear that the titanium dioxide coating deposited on the surface of the FSTCu particles did not form a complete coverage (refer to Fig. 3). The deposition of a patchy TiO_2 coating meant that a fraction of the SiO_2 surface was exposed. This would lead to a decreased photoactivity in terms of a reduction in the number of available active surface sites when compared with FSTH in which the surface was completely covered with titanium dioxide (refer to Fig. 2). Hence there is the opportunity to further improve the performance of these particles FSTCu by obtaining a complete coverage of the magnetic core's surface with the nano- TiO_2 crystals.

The second postulation is with regards to the degree of crystallinity of the titanium dioxide phase present in the sample FSTCu. Recalling that the titanium dioxide deposited was formed at a lower reaction temperature of 90 °C, it is thought that under these conditions the structure

of the titanium dioxide was not fully ordered but was rather in a transition region between amorphous and crystalline titanium dioxide. The preparation of partially crystalline titanium dioxide structure through the hydrolysis and condensation of a titanium alkoxide under mild heating conditions had also been confirmed by Terabe et al. [23] and Hague and Mayo [24]. Terabe et al. [23] used Raman spectroscopy to illustrate that the molecular structure of the amorphous precursors prepared using the sol–gel process approached that of the anatase phase with increased added water or acid addition [24].

In order to test this in our system, the prepared samples were subjected to further heat treatment at 60, 100 or 150 °C for 5 h in order to increase the degree of crystallinity of these samples. From the photoactivity results presented in Fig. 8, it can be clearly seen that the photoactivity increased as further heat was applied. We postulate that the increase in photoactivity with additional heat treatment is a result of increase in the crystallinity of the samples leading to a greater concentration of surface reactive sites. Our findings are in agreement with those reported by Abrahams et al. [14] who also observed a slow increase in the crystalline structure with increasing the temperature from 100 °C onwards [14]. Since in our system the optimum increase in photoactivity was found to occur with additional heat treatment at 100 °C, we deduce that the increase in crystallinity at temperatures of 60–150 °C is primarily due to the release of OH groups from the titanium dioxide structure. This is due to the fact that from our results, it was found that the sample additionally heat treated at 150 °C (sample FSTCu(150)) had the same photoactivity as that which was treated at 100 °C (sample FSTCu(100)). We envisage that the release of residual alkyl groups will occur at slightly higher temperatures. The formation of anatase structure at temperatures 150–190 °C has been reported by Yoldas [31] who also suggested that this may correspond to the release of residual organics which occurs at 185 °C. The increased degree in crystallinity will be verified by XRD analysis in future work.

From a qualitative comparison of the magnetic properties of the samples FSTCu and FSTH, the sample FSTCu was more magnetic. This is expected since the direct deposition of crystalline TiO₂ limited the oxidation of the magnetic core which would have otherwise occurred during calcination. The improved magnetic properties are critical to the application of the prepared particles as magnetic photocatalysts. The newly adopted methods also provided improvements in terms of shortening the time required for the preparation of the coated particles. This has practical consequences in terms of particle preparation. The lower energy input requirement due to the elimination of the high-temperature (450–550 °C) heat treatment step also has added cost benefits.

Another major advantage of the direct deposition of the nanosized crystalline TiO₂ nanocrystals onto the magnetic seed is that this approach opens up the possibility of taking advantage of the unique features of nanosized semiconductor particles, particularly their enhanced photoredox chem-

istry [17,32,33]. Nanosized particles, with diameters ranging between 1 and 10 nm, possess properties which fall into the region of transition between the molecular and the bulk phases [34]. As the bandgap of the semiconductor becomes larger with decreasing particle size, the band edges shift to yield larger redox potentials [35] and hence enhanced photoactivities.

5. Conclusions

In this paper, we have presented the results of a preliminary investigation aimed at investigating the direct deposition of nanosized crystalline titanium dioxide onto magnetic SiO₂/Fe₃O₄ seed particles. We have demonstrated the feasibility of directly coating nanocrystalline TiO₂ and applying them as photocatalysts.

While additional heat treatment was required to improve the crystallinity of the prepared samples, heating under mild conditions was sufficient to obtain high photoactivities while maintaining good separation properties. Thus the newly adopted particle preparation method is very promising in terms of eliminating the heat treatment step at high temperatures (450 °C) usually required when applying the conventional sol–gel technique for particle coating. Current studies are focussed on improving the coating technique by identifying the right conditions to give a complete surface coverage of the core particles while improving the crystalline nature of the nanosized titanium dioxide deposited.

References

- [1] P. Gherardi, E. Matijevic, Interactions of precipitated hematite with preformed colloidal titania dispersions, *J. Colloid. Interf. Sci.* 109 (1) (1986) 57–68.
- [2] T. Ishikawa, E. Matijevic, Formation of monodispersed pure and coated spindle-type iron particles, *Langmuir* 4 (1988) 26–31.
- [3] B. Aiken, E. Matijevic, Preparation and properties of uniform coated inorganic colloidal particles. IV. Yttrium basic carbonate and yttrium oxide on hematite, *J. Colloid. Interf. Sci.* 126 (2) (1988) 645–649.
- [4] A. Quirantes, R. Plaza, A. Delgado, Static light scattering study of size parameters in core-shell colloidal systems, *J. Colloid. Interf. Sci.* 189 (1997) 236–241.
- [5] R.E. Partch, Y. Xie, S.T. Oyama, E. Matijevic, Preparation and properties of uniform colloidal particles VIII. Titanium nitride on silica, *J. Mater. Res.* 8 (8) (1993) 2014–2018.
- [6] M. Penpolcharoen, A. Amal, V. Chen, in: *Proceedings of CHEMECA'98: The 26th Australian Chemical Engineering Conference*, 28–30 September 1998, Port Douglas, Qld, Paper No. 222, 1998.
- [7] I. Hap, E. Matijevic, Preparation and properties of uniform coated inorganic colloidal particles. X. Manganese compounds on hematite, *J. Colloid. Interf. Sci.* 192 (1997) 104–113.
- [8] M. Ocana, W.P. Hsu, E. Matijevic, Preparation and properties of uniform coated inorganic colloidal particle. 6. Titania on zinc oxide, *Langmuir* 7 (1991) 2911–2916.
- [9] S. Pratsinis, W. Zhu, S. Vemury, The role of gas mixing in flame synthesis of titania powders, *Powder Technol.* 86 (1996) 87–93.
- [10] B. Xia, H. Huang, Y. Xie, Heat treatment on TiO₂ nanoparticles by vapour-phase hydrolysis, *Mater. Sci. Eng. B* 57 (1999) 150–154.

- [11] J. Ying, T. Sun, Research needs assessment on nanostructured catalysts, *J. Electroceram.* 1 (3) (1997) 219–238.
- [12] S. Castillo, M. Moran-Pineda, V. Molina, R. Gomez, T. Lopez, Catalytic reduction of nitric oxide on Pt and Rh catalysts supported on alumina and titania synthesized by the sol–gel method, *Appl. Catal. B* 15 (1998) 203–209.
- [13] M. Gopal, W.J. Moberly Chan, L.C. De Jonghe, Room temperature synthesis of crystalline metal oxides, *J. Mater. Sci.* 32 (1997) 6001–6008.
- [14] J. Abrahams, R.S. Davidson, C.L. Morrison, Optimization of the photocatalytic properties of titanium dioxide, *J. Photochem.* 26 (1984) 353–361.
- [15] B. Ohtani, Y. Ogawa, S.I. Nishimoto, Photocatalytic activity of amorphous-anatase mixtures of titanium(IV) oxide particles suspended in aqueous solutions, *J. Phys. Chem. B* 101 (1997) 3746.
- [16] D. Beydoun, R. Amal, G. Low, S. McEvoy, A preliminary investigation into the synthesis of titania-coated magnetite as a novel photocatalyst, in: *Proceedings of the Third World Congress on Particle Technology*, 6–9 July 1998, Brighton, UK, Paper No. 385, 1998.
- [17] D. Beydoun, R. Amal, G. Low, S. McEvoy, Role of nanoparticles in photocatalysis, *J. Nanoparticle Res.* 1 (4) (1999) 439–458.
- [18] D. Beydoun, R. Amal, G. Low, S. McEvoy, Occurrence and prevention of photodissolution at the phase junction of magnetite and titanium dioxide, *J. Mol. Catal. A: Chem.* 180 (2002) 193–200.
- [19] R. Amal, D. Beydoun, G. Low, S. McEvoy, A photocatalyst, Australian Patent Application No. PP9722, 1999.
- [20] R. Amal, D. Beydoun, G. Low, S. McEvoy, A photocatalyst, International Patent Application, PCT/AU00/00313 (2000).
- [21] D. Beydoun, R. Amal, G. Low, S. McEvoy, Novel photocatalyst: titania-coated magnetite—activity and photodissolution, *J. Phys. Chem. B* 104 (18) (2000) 4387–4396.
- [22] T.D. Waite, in: M.F. Hochella, A.F. White (Eds.), *Reviews in Mineralogy*, Vol. 23, Mineralogical Society of America, Washington, DC, 1990, pp. 559–603.
- [23] K. Terabe, K. Kato, H. Miyazaki, S. Yamaguchi, A. Imai, Microstructure and crystallization behaviour of TiO₂ precursor prepared by the sol–gel method using metal alkoxide, *J. Mater. Sci.* 29 (1994) 1617–1622.
- [24] D. Hague, M. Mayo, Controlling crystallinity during processing of nanocrystalline titania, *J. Am. Chem. Soc.* 77 (7) (1994) 1957–1960.
- [25] H.D. Nam, B.H. Lee, S.J. Kim, C.H. Jung, J.H. Lee, S. Park, Preparation of ultrafine crystalline TiO₂ powders from aqueous TiCl₄ solution by precipitation, *Jpn. J. Appl. Phys.* 37 (1998) 4603–4608.
- [26] T. Sugimoto, E. Matijevic, Formation of uniform spherical magnetite particles by crystallization from ferrous hydroxide gels, *J. Colloid. Interf. Sci.* 74 (1) (1980) 227–243.
- [27] D. Beydoun, Development of a novel magnetic photocatalyst: preparation, characterisation, and implication for organic degradation in aqueous systems, Ph.D. Thesis, University of New South Wales, Sydney, NSW, 2000.
- [28] A. Garg, E. Matijevic, Preparation and properties of uniformly coated inorganic colloidal particles. 2. Chromium hydrous oxide on hematite, *Langmuir* 4 (1988) 38–44.
- [29] J.L. Look, C.F. Zukoski, Alkoxide-derived titania particles: use of electrolytes to control size and agglomeration levels, *J. Am. Chem. Soc.* 75 (6) (1992) 1587–1595.
- [30] A. Hanprasopwattana, Srinivasan, A. Sault, Datye, Titania coatings on monodisperse silica spheres (characterization using 2-propanol dehydration and TEM), *Langmuir* 12 (1996) 3173–3179.
- [31] B.E. Yoldas, Hydrolysis of titanium alkoxide and effects of hydrolytic polycondensation parameters, *J. Mater. Sci.* 21 (1986) 1087–1092.
- [32] N. Serpone, D. Lawless, E. Pelizzetti, Subnanosecond characteristics and photophysics of nanosized TiO₂ particulates from $R_{\text{part}} = 10\text{Å}–34\text{Å}$: meaning for heterogeneous photocatalysis, in: E. Pelizzetti (Ed.), *Fine Particles Science and Technology*, Kluwer Academic Publishers, Dordrecht, 1996, pp. 657–673.
- [33] J.M. Nedeljkovic, M.T. Nenodovic, O.I. Micic, A.J. Nozik, Photochemical kinetics of ultra-small semiconductor particles in solution: effect of size on the quantum yield of electron transfer, *J. Phys. Chem.* 90 (1986) 12.
- [34] D.W. Bahnemann, D. Bockelmann, R. Goslich, M. Hilgendorff, D. Weichgrebe, in: D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993, pp. 301–319.
- [35] R.F. Howe, M. Gratzel, EPR study observation of trapped electrons in colloidal TiO₂, *J. Phys. Chem.* 89 (1995) 4495.